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ZrO_2 promoted with sulfate, iron and manganese: a solid superacid catalyst capable of low temperature *n*-butane isomerization

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A sulfated oxide of zirconium, iron and manganese is prepared and shown to isomerize *n*-butane to isobutane at 35°C with rates approximately 2–3 orders of magnitude greater than sulfated zirconia as claimed by workers at Sun Refining and Marketing Company. Temperature programmed desorption of benzene is used to investigate the acidity of this remarkable catalyst. Adsorbed benzene is oxidized to CO_2 by the triply promoted oxide catalyst; CO_2, SO_2 and O_2 are found to desorb at 525, 575 and 560°C, respectively. Sulfated zirconia does not adsorb benzene in a similar manner. The results from the temperature programmed desorption of benzene cannot be correlated with the *n*-butane isomerization activity.

Keywords: Solid superacids; zirconium oxide; temperature programmed desorption; sulfated zirconia; butane isomerization

1. Introduction

Sulfated metal oxides have long been known to be solid superacids. For example, Hino and co-workers impregnated amorphous zirconium hydroxide with sulfuric acid to give upon calcination a solid superacid (Hammett acidity < -16) capable of catalyzing the isomerization of *n*-butane [1,2]. Much of the early enthusiasm for sulfated oxide, solid acids has declined due to the lack of stability in these types of materials. However, Hsu et al. have recently reported that a Fe and Mn promoted, sulfated ZrO_2 catalyst shows higher stability than sulfated ZrO_2 and that this new catalyst can isomerize *n*-butane at near room temperature with a rate three orders of magnitude greater than sulfated zirconia [3,4]. Additionally, Lin and Hsu published a new approach for detecting superacidity on solid superacids

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by using temperature programmed desorption (TPD) of substituted benzenes [5]. The objective of our work is to investigate the remarkable claims of Hsu and co-workers.

2. Experimental

Ammonia (28%, Baker) was added dropwise to a solution of $ZrOCl_2 \cdot 8H_2O$ (99.5%, Aldrich) until the pH = 10. The precipitated gel (zirconium hydroxide) was washed thoroughly with deionized water, filtered, dried overnight at 110°C and crushed to below 180 μm. Three solutions, 0.15 M $Mn(NO_3)_2$, 0.30 M $Fe(NO_3)_3$ and 3 wt% SO_4^{2-} were prepared by dissolving the appropriate amounts of $Mn(NO_3)_2 \cdot 9H_2O$, $Fe(NO_3)_3 \cdot 6H_2O$ and $(NH_4)_2SO_4$ (all purchased from Aldrich) in de-ionized, doubly-distilled water. Manganese, iron and/or sulfate were impregnated one at a time into the dried $Zr(OH)_4$ by stirring (1 min) and soaking (14 min) 1 g of solid in 1.5 ml of solution. The impregnating solution was removed by filtration and the solid was dried for several hours. This procedure is similar to that employed by Hsu et al. All solids used in this investigation are labeled by their composition (S – sulfate, F – iron, M – manganese, Z – zirconium oxide) with the letters in reverse chronological order of impregnation, i.e., SMZ is zirconium hydroxide impregnated first with manganese and then with sulfate. The solids were then calcined in flowing dry air at 650°C (3 h) except for SFMZ-750 which was calcined at 750°C for 1 h.

The sulfur, iron and manganese compositions of the various samples calcined to 500°C in air were analyzed at Galbraith Laboratories (Knoxville, TN). The samples had various sulfur, iron and manganese contents and the compositions are given in table 1. SSFMZ refers to SFMZ impregnated twice with sulfate solution. Surface areas (BET) were measured by the adsorption of N_2 using an Omnisorp 100 apparatus (Omicron Technology).

The isomerization of *n*-butane to isobutane was carried out in a flow-type,

Table 1

Elemental composition of samples. Samples were calcined in flowing dry air at 500°C for 4 h and then exposed to ambient conditions prior to analysis

Sample	Composition (wt%)			
	sulfur	iron	manganese	H_2O [a]
SFMZ	1.4	1.1	0.5	17.5
SZ	0.7	–	–	17.4
SFZ	1.4	1.2	–	18.5
SMZ	0.9	–	0.6	17.0
SSFMZ	1.9	1.1	0.5	15.5

[a] From thermogravimetric analysis.

fixed-bed reactor at 35°C and ambient pressure. 0.5 g of the as-synthesized sample was calcined (650°C, 3 h) and cooled under dry air flow in the reactor. The calcined sample was then reacted with a mixture of 19.98% *n*-butane and 80.02% helium (Matheson) flowing at 5 cm^3/min. The product gases were analyzed using an on-line HP 5890 Series II gas chromatograph containing a 50 m HP-1 crosslinked methyl-silicone gum column.

TPD experiments (similar to those performed by Lin and Hsu [5]) were conducted in a flow-type, fixed-bed reactor at ambient pressure. 0.3 g of the as-synthesized sample were calcined and cooled in situ to 100°C under dry air flow. Dry helium (6 ℓ/h) was used to sweep benzene vapor over the calcined sample (at 100°C) for 30 min. During this time the equivalent of 30 μl of liquid benzene were introduced into the TPD system. The dry helium flow was continued for an additional 30 min to allow removal of any physisorbed benzene. Desorption was conducted under the same helium flow by raising the temperature of the reactor at a rate of 15°C/min to the desired maximum desorption temperature (~ 800°C). The desorbed gases were analyzed with a thermal conductivity detector (TCD) and a Dycor M200M Quadrupole Gas Analyzer (MS). We observed m/e ratios of 32, 44, 64 and 78 which were assigned to O_2, CO_2, SO_2 and C_6H_6, respectively.

3. Results

All SFMZ samples tested for catalytic activity turned gray after calcination and were the tetragonal form of zirconia (identified by X-ray powder diffraction). Surface areas (BET) of the SFMZ samples before reaction were approximately 150 m^2/g.

The catalytic data observed from several of the samples are shown in fig. 1. SZ did not show appreciable activity at 35°C. It is clear that the incorporation of the transition metals has an effect on the catalytic activity such that the isomerization of *n*-butane occurs even at 35°C. Because of the temperature dependence of the *n*-butane–isobutane equilibrium, low temperature isomerization of *n*-butane is of practical importance.

The benzene TPD data from SFMZ and SZ are shown in fig. 2. Comparison of the TCD profiles with those published previously [5] suggests that the SFMZ produced here is the same as the samples prepared by Hsu et al. The first TCD peak corresponds to the desorption of benzene (and CO_2 in the case of SZ) and the high temperature peak is from SO_2 and O_2. With SFMZ, an additional peak appears at 540°C due to CO_2, SO_2 and a very small amount of O_2. There is clearly no high temperature benzene desorption. Fig. 3 shows the benzene TPD analysis from the TCD for SFMZ, SSFMZ, SFZ, SMZ, SFMZ-750, and SFMZ-750 without adsorbate and SZ. The peak temperatures for C_6H_6, SO_2, CO_2 and O_2 desorption for several TPD experiments are given in table 2.

Fig. 4 illustrates the TPD profiles from freshly calcined SFMZ and SFMZ that

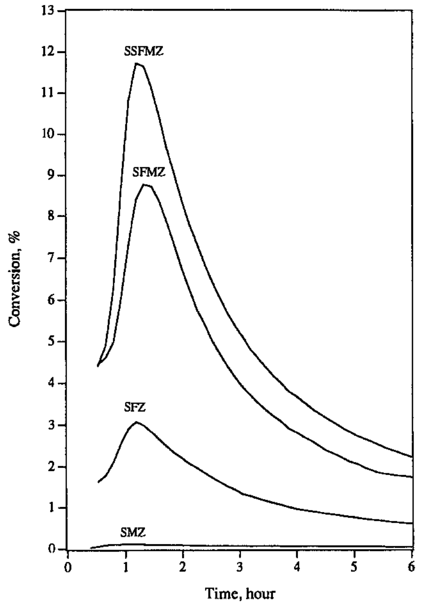

Fig. 1. Catalytic activity of SSFMZ, SFMZ, SFZ, and SMZ. Reactions conducted at 35°C and 1 atm using 0.5 g of catalyst calcined in dry air at 650°C for 3 h.

has been exposed to the *n*-butane reaction environment at 35°C for 1 h prior to the adsorption of benzene at 100°C. These data show that there are differences between the "fresh" surface and the surface in its most active form (see fig. 1).

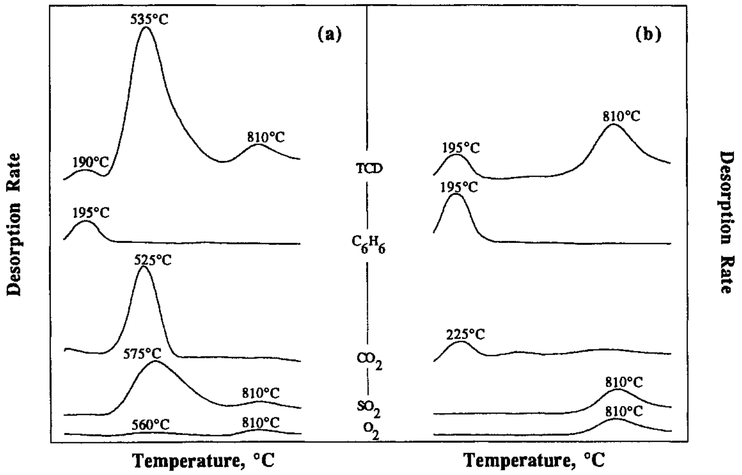

Fig. 2. Temperature programmed desorption (benzene) profiles from (a) SFMZ and (b) SZ using TC and MS detection. Samples (0.3 g) calcined in dry air at 650°C for 3 h.

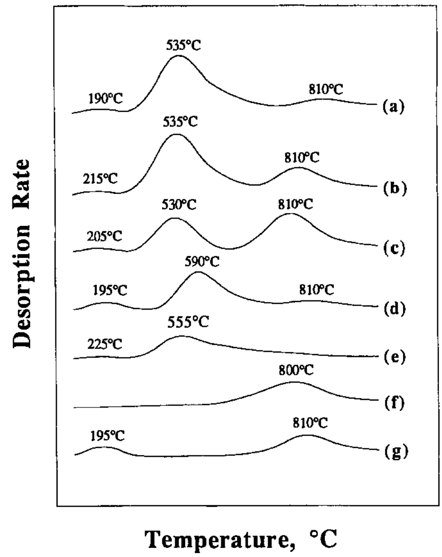

Fig. 3. Temperature programmed desorption (benzene) profiles from (a) SFMZ, (b) SSFMZ, (c) SFZ, (d) SMZ, (e) SFMZ-750 and (f) SFMZ-750 without adsorbate and (g) SZ using TC detection. Samples (0.3 g) calcined in dry air at 650°C for 3 h (a, b, c, d, g) or at 750°C for 1 h (e, f). Scale is the same in all profiles.

4. Discussion

Hsu et al. prepared a sulfated oxide containing iron, manganese and zirconium (SFMZ) that contained 1.5 wt% Fe, 0.5 wt% Mn and 1.4 wt% sulfur that was grey after calcination and had a surface area of 97 m^2/g. This solid was able to isomerize *n*-butane to isobutane at 27°C and gave a TPD peak at 562°C from benzene

Table 2
Desorption temperatures for benzene, carbon dioxide, sulfur dioxide and dioxygen from various samples exposed to benzene vapor

Sample	Desorption temperatures (°C)					
	C_6H_6	CO_2	SO_2		O_2	
			peak 1	peak 2	peak 1	peak 2
SFMZ	195	525	575	810	560	810
SSFMZ	200	515	580	810	580	810
SFZ	185	500	540	800	530	800
SMZ	195	570	620	810	615	810
SFMZ-750	225	535	625	–	–	–
SFMZ-750 [a]	–	–	–	800	–	800

[a] No benzene was adsorbed onto the sample prior to the TPD.

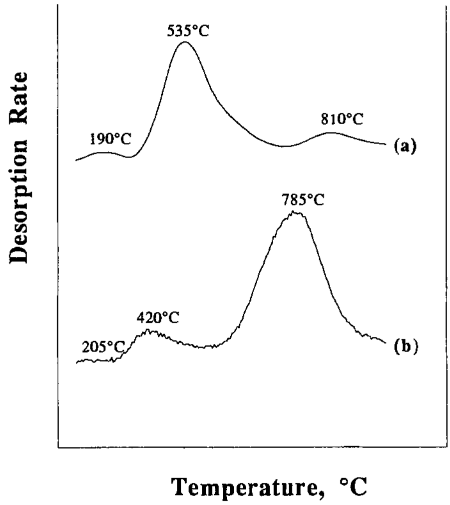

Fig. 4. Temperature programmed desorption (benzene) profiles from (a) freshly calcined SFMZ and (b) SFMZ exposed to flowing *n*-butane at 35°C for 1 h prior to benzene adsorption at 100°C using TC detection. Scale is the same in both profiles.

adsorbed at 100°C. The data shown here in figs. 1 and 2 reveal that we have been able to reproduce the behavior observed by Hsu et al. for SFMZ. Additionally, our elemental compositions are similar to those reported by Hsu et al. [3] and Lin and Hsu [5].

The catalytic activity of SFMZ is remarkable. At the conditions listed in fig. 1, SZ essentially does not isomerize *n*-butane (conversion less than 0.1%). The addition of either Fe or Mn increases the catalytic activity with the Fe impregnated sample (SFZ) showing an order of magnitude greater activity than the Mn impregnated material (SMZ). The combination of Fe and Mn enhances the catalytic activity over the singly impregnated solids, and the sulfate concentration plays an important role in optimizing the activity of the doubly impregnated zirconia (compare SFMZ to SSFMZ). It has been reported previously that the catalytic activity of SZ and SFMZ are dependent on sulfate concentration [5]. Thus, the lack of activity of SZ at 35°C could be due to the low sulfate concentration (see table 1). However, when the sulfur concentration was increased to 1.4 wt% (sulfate added via an incipient wetness procedure) the activity of SZ at 35°C was still below that shown in fig. 1 for SMZ. At this time, we have not found the optimum sulfate concentration for SFZ and SMZ. Thus, the activity differences observed in fig. 1 between SFZ and SMZ may be due to the variations in sulfate concentration (table 1). Hsu et al. report activity loss with time on-stream and extrapolated to zero time in order to compare the activities from different catalysts [3]. The data shown in fig. 1 reveal that this type of extrapolation is not possible. However, if we compare the maximum conversion from SFMZ and SZ at temperatures between 35 and 60°C, we confirm the conclusions of Hsu et al. concerning the fact that SFMZ is somewhere between two and three orders of magnitude more active than SZ. Additionally, in our hands, SFMZ reveals approximately 70% of its original activity after being regenerated by calcination in air, while SZ shows only about 25% (larger error in this value due to the very small levels of conversion being measured).

The TCD profiles in fig. 2 reproduce those reported by Lin and Hsu [5]. Here we provide further information concerning the nature of the desorbing species by on-line mass spectrometer analyses. Lin and Hsu correctly identified the high and low temperature desorptions as originating from sulfate decomposition (SO_2 and O_2) and weakly held benzene desorption, respectively. The peak observed from SFMZ at 535°C was claimed to be from strong acid sites capable of adsorbing a weak base, e.g., benzene. The nature of the desorbing species was not clarified. Here, we see that this desorption is from the combination of CO_2 (presumably from the total oxidation of benzene and oxygen from the solid), SO_2 and a very small amount of O_2. Since this peak does not appear in samples not exposed to benzenes, it is clear that the CO_2 originates from the benzene. Thus, SFMZ is capable of adsorbing benzene at sites not present (or present in extremely small amounts) in SZ. If these sites are acid sites as concluded by Lin and Hsu, they do not allow for the desorption of intact benzene at elevated temperatures. We are currently exploring the mechanism of the conversion of benzene to CO_2.

The TPD profiles shown in figs. 2 and 3 and desorption peaks listed in table 2 illustrate that CO_2, SO_2 and O_2 are liberated from SFMZ, SFZ and SMZ in the temperature range of 500–615°C. The important point is that SFMZ, SFZ and SMZ all give three TCD peaks while SZ does not. By comparing the peak temperatures and areas with the conversion data shown in fig. 1, it is clear that there is no correlation between the TCD peak (area or temperature) and the catalytic activity. Lin and Hsu claimed that there is a correlation between the peak area and the *n*-butane isomerization activity for a series of SFMZ catalysts in which the sulfate concentration was varied. We have not obtained enough information at this time to verify their correlation. It is not surprising that a correlation between the TPD data of the freshly calcined samples and their catalytic activity cannot be obtained in view of the transient catalytic behavior observed (fig. 1). In fig. 1, it is shown that the maximum conversion is observed at around 1 h on-stream at our conditions. We stopped the reaction at 1 h with a sample of SFMZ and then adsorbed benzene at 100°C and conducted the TPD (all performed in situ). The TPD results from this analysis are shown in fig. 4. As with "fresh" SFMZ, the reacted SFMZ sample shows three peaks in the TPD that are composed of the same species as described previously. Interestingly, the desorption temperatures are shifted to lower values for the second and third peaks and the intensity of the third peak is much larger than the second. At this time we are unable to identify the exact nature of the differences in the "fresh" and reacted SFMZ. However, it is clear that these two samples are significantly different suggesting that the physicochemical properties of the freshly calcined sample may not be representative of those of the working catalyst. Thus, we believe that the existence of the TPD peak around 530°C is characteristic of Fe and/or Mn impregnated, sulfated zirconias; however, it provides little insight into the catalytic activity obtained from these solids.

The data illustrated in figs. 3a, 3e and 3f show that the calcination temperature dramatically alters the nature of the catalyst. Notice that calcination at 750°C eliminates the high temperature sulfate decomposition peak from the sample exposed to benzene. This result suggests that there is a distribution of acid sites on the SFMZ and that calcination at 750°C eliminates sites that do not react with benzene (calcination at 650°C gives an 810°C sulfate decomposition peak where calcination at 750°C does not). The catalytic activity of SFMZ calcined at 750°C is less than that obtained when the sample is calcined at 650°C. Thus, no conclusions regarding the assignment of the catalytically active sites to specific desorption peaks can be made at this time. Currently, we are investigating this new and remarkable catalyst by numerous physicochemical characterization techniques. An important question that remains is what is the nature of the active site capable of isomerizing *n*-butane at room temperature?

5. Conclusions

We have independently verified that sulfated zirconia promoted with iron and manganese is capable of isomerizing *n*-butane to isobutane at near room temperature with rates approximately 2–3 orders of magnitude greater than sulfated zirconia as claimed by Hsu et al. [3]. We have not been able to correlate the TPD peak at ~ 560°C from SFMZ samples exposed to benzene to the catalytic activity as suggested by Lin and Hsu [5]. Additionally, we have shown that this TPD peak is from CO_2, SO_2 and O_2 indicating that the adsorbed benzene is totally oxidized on the catalyst samples.

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